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Manuscript title: A Geochemical Modelling of Multi-minerals Evolution for a 15 Months Experiment

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Abstract

The impact of hyper alkaline leachate released from the cementitious barrier of a geological disposal facility (GDF) on the host rock is a significant issue for the safety assessment of long-term nuclear disposal. However, modelling of multi-mineral transformations, multiple chemical reactions and multiple secondary phase pathways remains a challenge due to uncertainties in parameters and a limited available database describing the kinetics of dissolution/precipitation reactions. In this study a new modelling approach, Mixed Kinetic-Equilibrium (MKE), has been employed to study the complex reactions occurring in an experimental system consisting of Borrowdale Volcanic Group rocks permeated with a hyper-alkaline leachate over 15 months. The modelling suggests that dissolution of primary dolomite, quartz, calcite and K-feldspar in the host rock initially drives the chemical evolution of this system. The subsequent precipitation of several secondary phases, including calcite, brucite, talc and calcium-silicate-hydrate (CSH) phases, is predicted to control the long-term chemical equilibria and mineralogical composition of the host rock impacted by the alkaline leachate. The results from the modelling provides a deeper understanding of the long-term interactions between the host rock and high pH leachate, with dolomite predicted to be a major controlling phase on the geochemical evolution of the system.

Notation

A_0	Initial Surface area
$f_{H^+}, f_{H_2O}, f_{OH}, f_{CO_2}$	Inhibition factors
$\frac{IAP}{K}$	Ion activity divided by equilibrium constant, equal to the saturation ratio (SR) of the reactant
k_k	Reactant empirical constant
$k_{H^+}, k_{H_2O}, k_{OH^-}, k_{CO_2}$	Solutes rate coefficients
k_1, k_2, k_3, k_4	Rate constants
m_k	Moles of reactant at a given time
m_{0k}	Initial moles of reactant
n	Order of reaction constant (Crystal grain size distribution)
P_{CO_2}	Partial pressure of carbon dioxide
R_k	Reactant overall dissolution rate
r_k	Reactant specific reaction rate
r_f	Forward reaction
SI	Saturation index
SR	Saturation ratio
V	Solution volume
$[X]$	Ion activity of the element X

Introduction

In the UK the concept of multilayer barrier developed by Nirex (Francis et al., 1997) has been adopted for intermediate/low level waste disposal. A location hundreds of meters below the biosphere is to be selected for a deep geological waste repository, with wastes interred within stainless-steel containers encapsulated within a cementitious engineered barrier at the site. A hyper-alkaline plume may be generated by groundwater in contact with the cement barrier, creating a chemical disturbed zone (CDZ) (Chen et al., 2015, Chen et al., 2016, Chen and Thornton, 2018, Corkhill et al., 2013). The influence of the CDZ on the host rock for an intermediate/low level waste disposal facility in the UK has been summarized in the BIGRAD report (Small et al., 2016). In addition, significant effort has been made by the wider waste management community in the past two decades, in terms of experimental analysis (at lab scale, field scale and on natural analogues), as well as in terms of modelling, to investigate the long-term interaction between cement materials and potential host rock. The mechanisms and modelling of waste-cement and cement-host rock interactions have been summarized in a special issue of Physics and Chemistry of the Earth (Jacques et al., 2014).

In the field of geochemical modelling considerable research has been conducted based on the concept of thermodynamic equilibrium (Westall, 1986, Bethke, 1994, Bethke, 1996, Van der Lee, 1997). However, in a disposal site with natural water dominant, this assumption may not be valid for slow reaction processes. Therefore, an improved modelling approach incorporating non-equilibrium and kinetically controlled precipitation and dissolution was developed by (Soetaert et al., 1996) to illustrate kinetics processes in terms of first or second

order formulations. However, even with this model, values of kinetic parameters such as surface area, initial and final moles of reactants, reaction and precipitation rates cannot easily be obtained from experimental study. For example, (Parkhurst and Appelo, 1999) have attempted to address this using the geochemical model of PHREEQC as the framework for the complex geo-reaction system, however the database only covers a rates for a limited number of minerals such as calcite and K-feldspar, for example.

Recently, a Mixed Kinetic-Equilibrium approach (MKE) was introduced to combine the advantages of both kinetic and equilibrium laws and enable modelling of very complex multi-mineral and multi-component reaction systems (Chen and Thornton, 2018, Van der Lee, 1998, Bethke, 1996). The new approach enables faster reactions using the equilibrium concept with slower kinetically-limited reactions. In addition, it allows existing models developed on the thermodynamic equilibrium approach to be re-evaluated. Nevertheless, this requires a full understanding of the chemical reaction system (e.g. which reaction is faster and slower, etc.) and the availability of appropriate kinetic data. This paper illustrates the application of the MKE approach in the interpretation of multi-mineral reactions that may occur in Borrowdale Volcanic Group rocks during experimental permeation with a model hyper-alkaline leachate originating from the cementitious barrier of a geological disposal facility for intermediate-level nuclear waste (ILW).

Experimental study

A 15 year experiment, starting in 1995, was conducted by the British Geological Survey (Rochelle et al., 2001, Moyce et al., 2014, Rochelle et al., 2016) to examine the chemical

behaviour of the Borrowdale Volcanic Group (BVG) rock sample in contact with young near-field porewater (YNFP) or evolved near-field groundwater (ENFG) intended to represent model fluid compositions released from cementitious barrier materials used for ILW disposal. The rock sample used in the experiment was taken from a hydrologically fracture zone in Ordovician volcanic rocks in the UK. A 150 ml and 100 ml pressure vessels were used for the solution with, and without, BVG rock, respectively.

The original 15 year experiment was divided into two time periods with different targets. The first period, from 0-15 months, investigated short term mineral evolution, whereas the second period, from month 15 to year 15, investigated the long-term mineral evolution. The modelling study described in this paper considers the first period of the experiment from 0 to 15 months, and is focused on chemical interactions occurring between the YNFP and BVG rock only (YNFP characteristics are given in Table 1).

Fluid and rock samples were collected from these vessels at 4, 9 and 15 months for chemical and mineralogical analysis. Before analysis, the rock samples were washed in isopropanol, milled and micro ionised in acetone with the addition of 10% corundum (Al_2O_3) as an internal standard. The rock samples were then placed in a stainless-steel holder and analysed using a PANalytical X'Pert Pro diffractometer. The final analysis process was then performed using the PANalytical X'Pert Highscore Plus software (Moyce et al., 2014, Rochelle et al., 2016). Other than the analysed samples, the experiment was continued in parallel for a much longer reaction period of 15 years (Moyce et al., 2014, Chen and Thornton, 2018).

Mineralogical analysis and kinetic information for BVG rock

The mineralogical composition of BVG rock is given in Table 2. Note here that the fracture fill and clay phases have not been considered despite that the starting material has indicated their presence. Six minerals are presented in BVG rock, all of which can dissolve and react with YNFP. Based on the mineral weight percentage values, the initial mass for each reactant is calculated for 35g of rock sample, based on the original experiment (Rochelle et al., 2016).

The overall dissolution rates of minerals may be described by (Appelo and Postma, 2005):

$$R_k = r_k \frac{A_0}{V}\left(\frac{m_k}{m_{0k}}\right)^n \qquad (1)$$

In which $\frac{A_0}{V}$ is initial surface area (m^2) / volume of solution (L), $\left(\frac{m_k}{m_{0k}}\right)^n$ is moles of solid at a given time / initial moles of solid, n=2/3 (for uniformly dissolving spheres and cubes, generally obtained from experiments), r_k is a specific reaction rate ($mol/m^2/s$) with various forms. The general formulation below is proposed by (Rimstidt and Barnes, 1980):

$$r_k = k_k\left(1 - \left(\frac{IAP}{K}\right)_k\right) \qquad (2)$$

Where k_k is an empirical constant for a reactant and $\left(\frac{IAP}{K}\right)$ (ion activity divided by equilibrium constant) is equal to the saturation ratio (*SR*) of the reactant. The kinetic information for the minerals in BVG rock obtained from the literature is summarised below, and the rates and surface areas used for the modelling are provided in Table 3.

Quartz (SiO_2)

The dissolution function of quartz may be described by (Merkel et al., 2005):

$$SiO_2 + 2H_2O \leftrightarrow H_2SiO_4 \qquad (3)$$

and, as per equation (1) and (2), the overall dissolution kinetic equation for quartz will be:

$$R_{Quartz} = k_{Quartz}\left(\frac{A_0}{V}\right)\left(\frac{m}{m_0}\right)^{0.67}\left(1-\left(\frac{IAP}{K}\right)_{Quartz}\right) \qquad (4)$$

where R is overall quartz dissolution rate (mol L^{-1} s^{-1}), A_0 is the initial surface area of quartz (m^2), V is the solution volume (L), m is the moles of quartz at a given time, m_0 is the initial moles of quartz ; k is the specific dissolution rate = $10^{-12.2}$ mol/m^2/s at 70°C (Worley, 1994), $\left(\frac{IAP}{K}\right)$ is equal to the *SR* value of quartz.

Orthoclase ($KAlSi_3O_8$) K-feldspar

K-feldspar ($KAlSi_3O_8$), also known as orthoclase, is 12% of the BVG rock. Preliminary rate expressions for K-feldspar may be found in the literature (Sverdrup, 1990, Brantley et al., 1993). The general form of the overall dissolution rate proposed by (Appelo and Postma, 2005) is used to simulate K-feldspar reaction at specific temperatures and pH value:

$$R_{K-feldspar} = k_{K-feldspar}\left(\frac{A_0}{V}\right)\left(\frac{m}{m_0}\right)^{0.67}\left(1-\left(\frac{IAP}{K}\right)_{K-feldspar}\right) \qquad (5)$$

where

$$k_{K-feldspar} = k_{H^+}\frac{[H^+]^{0.5}}{f_H} + k_{H_2O}\frac{1}{f_{H_2O}} + k_{OH^-}\frac{[OH^-]^{0.3}}{f_{OH}} + k_{CO_2}\frac{[P_{CO_2}]^{0.6}}{f_{CO_2}} \qquad (6)$$

where $k_{K-feldspar}$ is the specific reaction rate (mol m^{-2} s^{-1}), k_i are the solute rate coefficients (mol m^{-2} s^{-1}), and f_i are inhibition factors.

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Calcite ($CaCO_3$)

(Appelo and Postma, 2005, Parkhurst and Appelo, 1999, Plummer et al., 1978) have described the dissolution rate of calcite in a solution using the following expression which is suitable for both dissolution and precipitation reaction:

$$r_{calcite} = \underbrace{k_1[H^+] + k_2[H_2CO_3] + k_3[H_2O]}_{r_f} - k_4[Ca^{2+}][HCO_3^-] \qquad (7)$$

and then simplified in a calcite-water system as:

$$r_{calcite} = r_f \left[1 - \left(\frac{IAP}{K}\right)^{2/3}_{Calcite}\right] \qquad (8)$$

The overall dissolution rate of calcite will then be:

$$R_{calcite} = r_{calcite}\left(\frac{A_0}{V}\right)\left(\frac{m}{m_0}\right)^{0.67} = r_f \left(\frac{A_0}{V}\right)\left(\frac{m}{m_0}\right)^{0.67}\left[1 - \left(\frac{IAP}{K}\right)^{2/3}_{Calcite}\right] \qquad (9)$$

The value of the coefficients k_1, k_2 and k_3 in equation (7) are obtained from the literature (Plummer et al., 1978).

Dolomite $CaMg(CO_3)_2$

The dissolution kinetics of dolomite has been analysed by (Busenberg and Plummer, 1982) and found to be much slower than that for calcite. The rate expression for dolomite dissolution may also be found from the saturation index $\left(SI = log\left(\frac{IAP}{K}\right)\right)$, as below (Appelo and Postma, 2005, Parkhurst and Appelo, 1999, Appelo et al., 1984):

$$R_{Dolomite} = -k_{Dolomite}\left(\frac{A_0}{V}\right)\left(\frac{m}{m_0}\right)^{0.67} log\left(\frac{IAP}{K}\right)_{Dolomite} \qquad (10)$$

Hematite (Fe_2O_3) *and Muscovite* [$KAl_3Si_3O_{10}(OH)_2$]

The dissolution behaviour of hematite (Fe_2O_3) has been investigated intensively in low pH conditions (Sidhu et al., 1981, Schwertmann, 1984, Torrent et al., 1987). However, few studies have been done at high pH. The dissolution kinetics of muscovite has been discussed by (Knauss, 1989) as a function of pH and time. Since the percentage of hematite in the rock sample is very low (2%) and it does not present significant influence on the mineral evolution process in the experiment (Rochelle et al., 2016), and muscovite (a clay mineral presented in the fracture of the BVG rock) has not been the attention of the initial experiment (Rochelle et al., 2001, Moyce et al., 2014), therefore both phases are not modelled to simply the discussion.

Modelling methodology

Conceptual model

PHREEQC, a geochemical modelling tool developed by the USGS (U.S. Geological Survey) (Parkhurst et al., 1980) with functions such as aqueous, mineral, surface-complexion, and ion-exchange equilibrium, etc, was used with a modified database (entitled as llnl-BGS) that included additional kinetic information based on the LLNL (Lawrence Livermore National Laboratory) aqueous model parameters database. Thermodynamic information (reactions and equilibrium constants) for the major minerals is included in Table 4 of the appendix (Chen and Thornton, 2018). Note here that there are other databases available, such as Thermoddem and Thermoddem DB (Blanc et al., 2012) for low temperature water/rock interactions and waste materials, and CEMDATA DB (Lothenbach et al., 2019) specifically for cement materials

supporting state-of-the-art models for C-A-S-H phases as solid solution (with variable C/S ratio). As this paper is focused on the mixed equilibrium and kinetics approach, and the control mineral function of dolomite, the modified PHREEQC database was used for convenience. The complex potential interactions between primary and secondary phases are described in Figure (1).

Figure (2) shows the modelling process developed in this study. Initially, a conceptual model was established based on information from both theoretical and experimental analysis. The kinetic information was obtained from published databases or literature. During this process reaction rates were compared in terms of the timescale, to identify the quickest or slowest rates of minerals and to provide supporting information for the modelling approach (e.g. either kinetics or equilibrium, or a mix of both). In the case where the kinetics of any minerals are not available, or there is a large difference between rates (e.g. more than 10^2), then the mixed kinetics and equilibrium approach may be preferred. Finally, potential secondary phases, obtained by using information from either the experiment or published literature, were used to refine the model.

Secondary phases

Over a long period several dissolution and precipitation reactions may occur as the chemical system evolves. The potential secondary phases selected in this study include brucite, talc, calcite and CSH phases, according to experimental observations and theoretical considerations of interactions between the host rock and cement leachate (Small et al., 2016). Although PHREEQC can represent the thermodynamics of brucite, talc and calcite equilibria, the

relevant data required to simulate CSH reactions is lacking. For this reason, more investigation needs to be performed on this topic.

$xCaO.ySiO_2.zH_2O$ can be used to describe the general CSH phase in which silicate in Portland cement reacts with water. The chemical reaction which will generate CSH phases is usually described as (Peterson et al., 2005):

$$2Ca_2SiO_4 + 5H_2O \rightarrow 3CaO.2SiO_2.4H_2O + Ca(OH)_2 + 58.6\ kJ \qquad (11)$$

More than 30 calcium silicate hydrate phases exist (also known as C-S-H or CSH) (Taylor, 1997). The structural complexity of this silicate makes it difficult to know the exact precipitated phase since the reactions will create several secondary phase compositions (Chen et al., 2004). For simplicity, tobermorite was selected to represent CSH phases since the ratio of Ca:Si was observed to be variable during the reaction in the experiment. The formation and precipitation of CSH phase are outside the scope of this study; for this the reader is referred to the original 15 years experiment study (Moyce et al., 2014, Chen and Thornton, 2018).

Results and discussion

Modelling of short-term experiment (0 months to 15 months)

Calcite, quartz, K-feldspar and dolomite have all been modelled in the first 15 months using the mixed equilibrium and kinetics approach. Changes in the concentration of Ca, Mg, Na, Si, CO_3 and pH, as measured from the experiment, were analysed in the modelling simulations.

Since all the 6 minerals involved in the dissolution do not contain Na+, and the potential secondary phases do not also consume Na^+, then Na^+ remains constant over time, in good agreement with the experimental results (Figure 3). Ca^{2+} decreases significantly in the initial

few months due to precipitation of $CaCO_3$ (Figure 4), which has a SI above zero (Figure 9). Silicon (Si) (Figure 5) increases due to dissolution of both quartz and K-feldspar (both have SI below zero as in Figure 9) and then decreases due to precipitation of talc and some CSH phases. The magnesium (Mg) in the original solution decreases before the fourth month (nearly matching the timing of peak Si values due to quartz dissolution) as a result of precipitation of secondary talc $[Mg_3Si_4O_{10}(OH)_2]$ and brucite $[Mg(OH)_2]$ phases (both have above zero SI at the beginning of the reaction, Figure 6 and 9). Carbon trioxide (CO_3) concentration increases in the solution as a result of dolomite dissolution (Figure 7). The pH decreases due to the precipitation of secondary phases (Figure 8) and may also subsequently influence the dissolution or precipitation of some secondary phases.

Figure 9 shows the evolution of some primary phases and selected secondary phases. As there was an initial concentration of Ca, CO_3 and Mg in the YNFP at time zero (Rochelle et al., 2016), dolomite $CaMg(CO_3)_2$, calcite ($CaCO_3$) and talc are oversaturated in the solution and hence start to precipitate during the initial few weeks. After some time, dolomite reaches a SI of 0 but then starts to dissolve, allowing other minerals to reach equilibrium. Since dolomite forms 29% of the BVG rock and can provides a pool of Ca, Mg and CO_3, calcite and talc both reach equilibrium, whereas dolomite will keep dissolving with a positive slope to reach equilibrium as well. Since the dissolution rate of dolomite is very small, its SI is below 0 until month 15 (Figure 9). As a CSH phase, tobermorite-11A is unlikely to precipitate due to a deficiency in Ca related to calcite precipitation. K-feldspar initially has a negative SI and then follows the dissolution kinetics to reach equilibrium.

From the analysis, dolomite is proved to be a major controlling phase on the geochemical evolution of BVG rock minerals interaction with the young cement leachate. The findings from the numerical modelling and theoretical analysis have provided an in-depth understanding of the long-term interactions between the host rock and alkaline leachate. The modelling results in line with experimental further support the concept of Mixed Kinetic-Equilibrium (MKE) approach to interpret the evolution of multiple mineral phases.

Limitations and challenges of modelling the experiment

Whether an experiment of this type can be modelled correctly by numerical methods depends on (1) the experimental data obtained, (2) the modelling tools and methods, (3) the theoretical analysis, and (4) the relationship between the experiment and modelling (some parameters might be important for modelling, however, is not necessary for experiment). One of the challenges of modelling this experiment was the unknown parameters, which was caused by the different scientific focus for the experiment. For example, the experimental study was focused on mineral evolution, instead of dissolution/precipitation kinetics, with no interest in dissolution parameters such as surface area. However, such information is essential for modelling dissolution kinetics. At least 3 parameters (e.g. empirical constant, initial surface area and moles of solids at a given time) may be needed to simulate the dissolution kinetics of one mineral; hence at least 18 uncertain parameters must be considered to model the reaction kinetics of 6 minerals in this study, a significant uncertainty. Such a challenge shows the importance of applying "mixed kinetics and equilibrium methods" to interpret the evolution of multiple mineral phases, which should be based on proper assumptions in order to achieve a

reasonably accurate prediction.

Conclusion

A new approach, "mixed kinetic and equilibrium method", has been implemented to model the reaction of Borrowdale Volcanic Group (BVG) rock in contact with Young Near-Field Porewater (YNFP) over 15 months. The aim was to study the influence of high pH alkaline leachate on the chemical dissolution of the host rock in a geological disposal facility. The results indicate that (1) dolomite equilibria will be the most significant control during the reaction of this pore fluid with the BVG rock, (2) Na is not involved in mineral alteration reactions, and (3) Ca^{2+} from dissolution of dolomite will be precipitated in the reaction, forming a variety of secondary mineral phases. Modelling multi-mineral evolution in the CDZ surrounding a nuclear waste geological disposal facility, characterised by both equilibrium and kinetic reactions, remains a challenging field. However, the results of this study suggest that the new approach adopted offers greater insight into the long-term interactions between the high pH alkaline leachate and host rock for this scenario.

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Appendix 1 Thermodynamic database

Table 4. Reactions and equilibrium constants for minerals used in the calculations

Mineral	Reaction	Log Keq
Calcite	$CaCO_3 + H^+ = Ca^{++} + HCO_3^-$	1.8487
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{+++} + 3SiO_2 + 6H_2O$	13.5858
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = +2Al^{+++} + 2SiO_2 + 5H_2O$	6.8101
Chalcedony	$SiO_2 = +1.0\ SiO_2$	-3.7281
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{:}6H_2O + 8H^+ = +4Mg^{++} + 6SiO_2 + 11H_2O$	30.4439
Brucite	$Mg(OH)_2 + 2H^+ = +1.0\ Mg^{++} + 2H_2O$	16.2980
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O + 12H^+ = +2Al^{+++} + 3SO_4^{--} + 6Ca^{++} + 38H_2O$	62.5362
Tobermorite-11A	$Ca_5Si_6H_{11}O_{22.5} + 10H^+ = +5Ca^{++} + 6SiO_2 + 10.5H_2O$	65.6121
Tobermorite-14A	$Ca_5Si_6H_{21}O_{27.5} + 10H^+ = +5Ca^{++} + 6SiO_2 + 15.5H_2O$	63.8445
Tobermorite-9A	$Ca5Si6H6O20 + 10\ H+ = +\ 5Ca++ + 6SiO2 + 8H2O$	69.0798
Portlandite	$Ca(OH)_2 + 2H^+ = +1.0Ca^{++} + 2H_2O$	22.5552
Gypsum	$CaSO_4{:}2H_2O = +\ 1.0\ Ca^{++} + 1.0\ SO_4^{--} + 2H_2O$	-4.4823
Hillebrandite	$Ca_2SiO_3(OH)_2{:}0.17H_2O + 4H^+ = SiO_2 + 2Ca^{++} + 3.17\ H_2O$	36.8190
Foshagite	$Ca_4Si_3O_9(OH)_2{:}0.5H_2O + 8H^+ = +3SiO_2 + 4Ca^{++} + 5.5H_2O$	65.9210

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Table 1. Recipes for young near-field porewater (YNFP) prepared by the British Geological Survey (Rochelle et al., 2016)

Chemical component	Concentration (mg/L)
Br	0.5
Ba	0.01
CO_3	166
Ca	51.8
Cl	63.7
F	19
Fe	0.1
K	3230
Mg	0.089
Mn	0.01
Na	1890
SO_4	1
NO_3	1
Si	9.2
Sr	0.018
pH (at 70ºC) *	11.67

* Adjusted using NaOH, 1.5137 g required for the YNFP

Table 2. Quantitative XRD analysis of unreacted BVG rock starting material conducted by the British Geological Survey (Rochelle et al., 2001, Rochelle et al., 2016). m_0 is calculated based on a 35g rock sample

Mineral	Weight %	m_0 (g)
Orthoclase	12	4.2
Quartz	41	14.35
Dolomite	29	10.15
Muscovite	13	4.55
Hematite	2	0.7
Calcite	3	1.05

Table 3. Modelling parameters for the BVG rock

Mineral	Weight %	Solution Volume (L)	Surface area (m^2/g)	Rate constant
Orthoclase	12		0.02 (De Windt et al., 2008)	k (using equation 6) (Appelo and Postma, 2005)
Quartz	41		0.02 (De Windt et al., 2008)	$k = 1x10^{-12.2}$ (70^oC) (Worley, 1994)
Dolomite	29	0.15 (Rochelle et al., 2016)	0.02 (De Windt et al., 2008)	$k= 1.2x10^{-10}$ (Appelo and Postma, 2005, Appelo et al., 1984). This value was lowered one order of magnitude to fit well with the experimental data ($k= 1.2x10^{-11}$)
Muscovite	13		NA	NA
Hematite	2		NA	NA
Calcite	3		0.02 (De Windt et al., 2008)	k1 = 10^(0.198 - 444.0 / (273.16 + T)) k2 = 10^(2.84 - 2177.0 / (273.16 + T)) k3 = 10^(-1.1 - 1737.0 / (273.16 + T)) in which T denotes temperature. (Appelo and Postma, 2005, Plummer et al., 1978)

Figure 1. Conceptual model for geochemical modelling of BVG reaction with YNFP

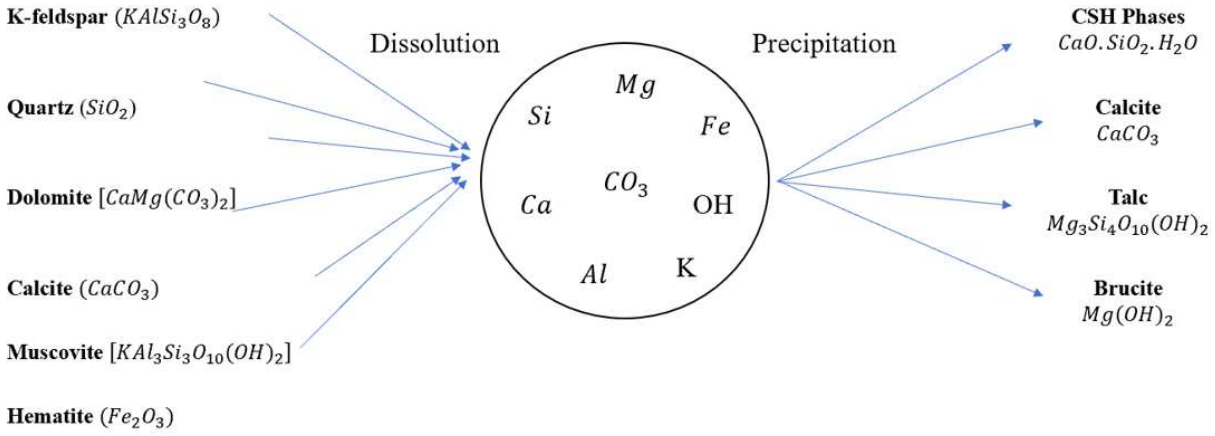

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Figure 2. Modelling process adopted

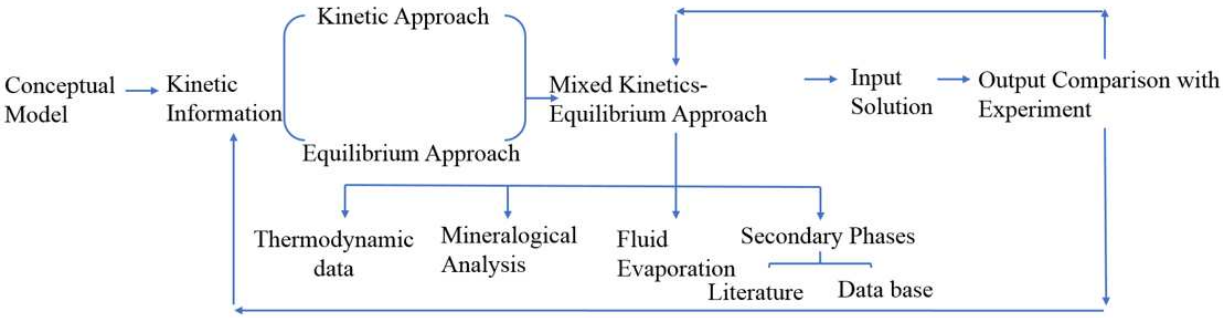

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Figure 3. Na concentration variation over time

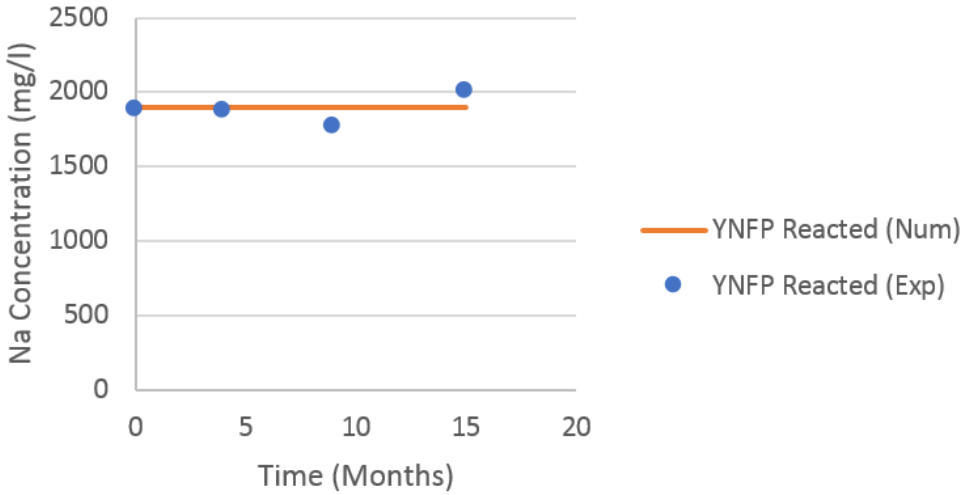

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Figure 4. Ca concentration variation over time

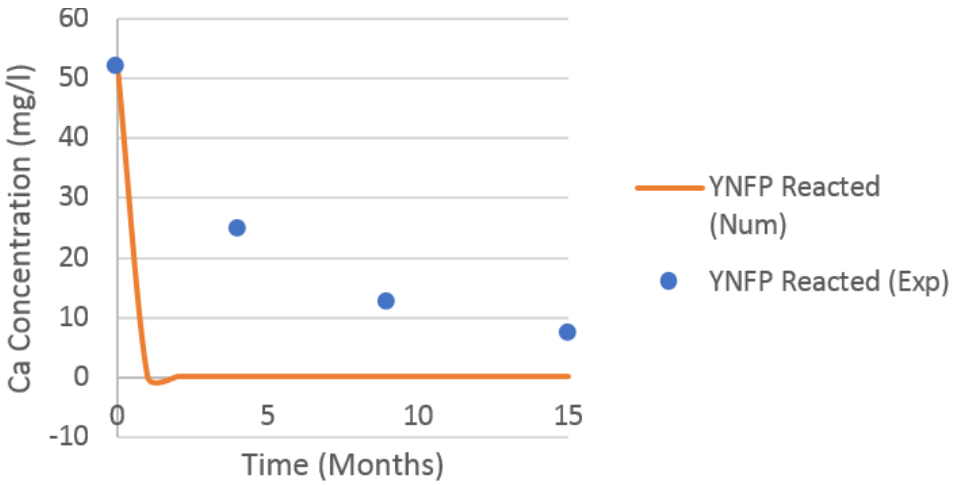

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Figure 5. Si concentration variation over time

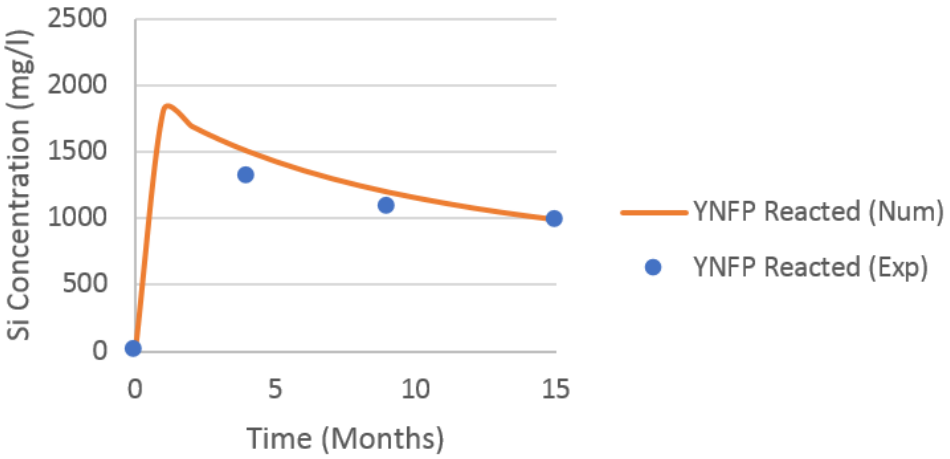

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Figure 6. Mg concentration variation over time

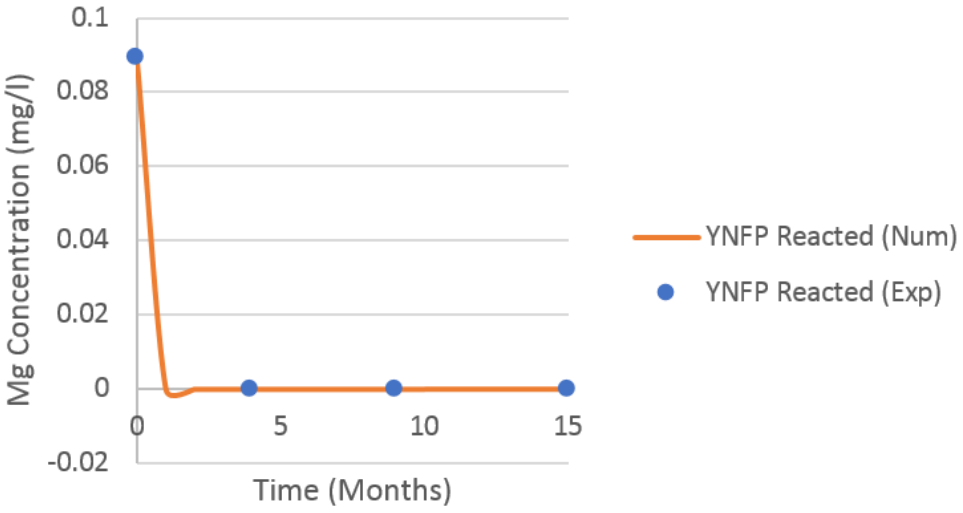

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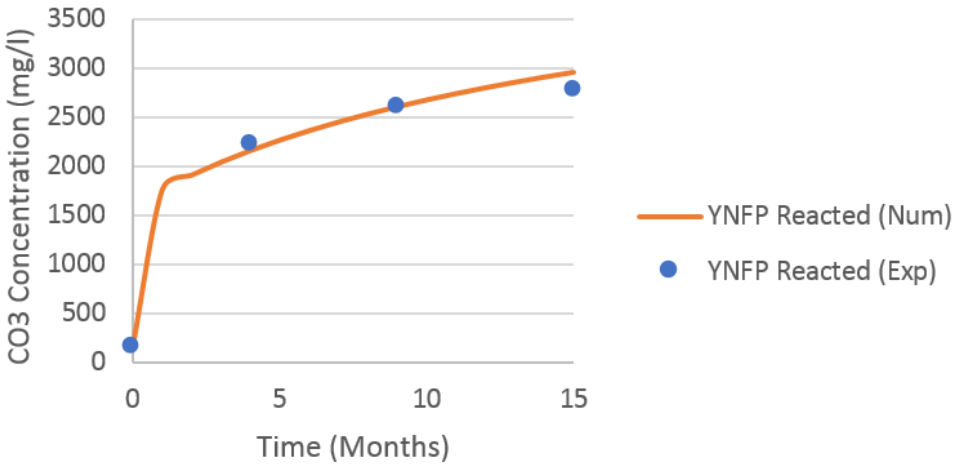
Figure 7. CO_3 concentration variation over time



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doi: 10.1680/jenge.19.00081

Figure 8. pH variation over time

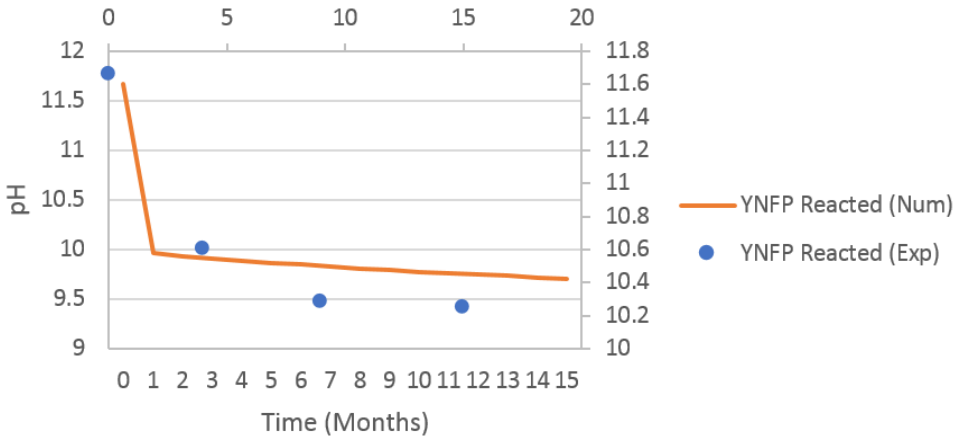

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Figure 9. Variation in minerals saturation indices (SI) over time